

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C07C 51/60, 51/58, 53/50, 55/40, 59/135, 51/215, 45/54, 49/175</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/25082</b> <b>(43) International Publication Date:</b> 21 September 1995 (21.09.95)
<b>(21) International Application Number:</b> PCT/US95/01995 <b>(22) International Filing Date:</b> 15 February 1995 (15.02.95)  <b>(30) Priority Data:</b> 08/213,109 15 March 1994 (15.03.94) US  <b>(71) Applicant:</b> MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).  <b>(72) Inventor:</b> MOORE, George, G., I.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).  <b>(74) Agents:</b> WEISS, Lucy, C. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		<b>(81) Designated States:</b> CN, JP, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR CONVERTING PERFLUORINATED ESTERS TO PERFLUORINATED ACYL FLUORIDES AND/OR KETONES  <b>(57) Abstract</b>  A process for converting perfluorinated carboxylic acid esters to perfluorinated acyl fluorides and/or perfluorinated ketones comprises the step of combining at least one perfluorinated carboxylic acid ester with at least one initiating reagent selected from the group consisting of gaseous, non-hydroxylic nucleophiles; liquid, non-hydroxylic nucleophiles; and mixtures of at least one non-hydroxylic nucleophile (gaseous, liquid, or solid) and at least one solvent which is inert to acylating agents. The process enables the dissociation of even high molecular weight, perfluorinated esters.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Licchtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

PROCESS FOR CONVERTING PERFLUORINATED ESTERS TO  
PERFLUORINATED ACYL FLUORIDES AND/OR KETONES

Field of the Invention

This invention relates to a process for preparing perfluorinated carboxylic acid fluorides and/or perfluorinated ketones.

Background of the Invention

Many products of commercial value (such as oil- and water-repellant finishes for textiles, paper, electronic articles, and the like; stain-repellant finishes for leather; and surfactants for a variety of applications) can be made from perfluorinated carboxylic acid fluorides (hereinafter, perfluorinated acyl fluorides) and perfluorinated ketones.

Perfluorinated acyl fluorides can be prepared by electrochemical fluorination (ECF) of the corresponding hydrocarbon carboxylic acid (or a derivative thereof), using either anhydrous hydrogen fluoride (Simons ECF) or  $KF \cdot 2HF$  (Phillips ECF) as the electrolyte. However, a drawback of Simons ECF is that side reactions often occur, and low purity and low yields are often obtained due to the formation of rearrangement and degradation products.

Perfluorinated acyl fluorides can also be prepared from telomers of tetrafluoroethylene, but a characteristic of this method is that a distribution of molecular weights is obtained.

Although Phillips ECF (KF.2HF) or direct fluorination (F<sub>2</sub>) can be employed to reduce the occurrence of side reactions and provide high yields of a desired fluorinated product, hydrocarbon carboxylic acids cannot be fluorinated by such techniques without undergoing decarboxylation and/or other side reactions. Hydrocarbon carboxylic acid fluorides are extremely water-sensitive and difficult to handle, and hydrocarbon carboxylic acid chlorides yield chlorine-substituted fluorochemical products. In contrast, hydrocarbon carboxylic acid esters function well as starting compounds in both fluorination processes (see, e.g., U.S. Pat. Nos. 3,900,372 (Childs et al.) and 5,093,432 (Bierschenk et al.)), but, when hydrocarbon carboxylic acid esters are fluorinated, perfluorinated carboxylic acid esters (rather than perfluorinated acyl fluorides) are obtained. The perfluorinated esters are less useful than the corresponding acyl fluorides or ketones as intermediates in the preparation of commercial products, because perfluorinated esters, upon reaction with nucleophiles such as methanol, provide mixtures of products (derived from the acyl and the alkoxide portions of the perfluorinated ester) which may be difficult to separate. The side reactions of perfluorinated esters are especially limiting in making condensation polymers from difunctionals. Additional steps must therefore be undertaken to convert the perfluorinated esters to the more useful perfluorinated acyl fluorides and/or ketones.

U.S. Pat. No. 3,900,372 (Childs et al.) describes a combination process for the conversion of primary or secondary alkanols to perfluorinated acyl fluorides and/or perfluorinated ketones wherein said alkanols

are esterified with acyl fluorides and the resulting partially fluorinated esters passed to an electrochemical fluorination step to produce perfluorinated esters which are thereafter cleaved on contacting with a source of fluoride ion under reacting conditions, e.g., a bed of a solid alkali metal fluoride catalyst at a temperature within the range of 80°C to 220°C.

De Marco et al. disclose (in J. Org. Chem. 37(21), 3332 (1972)) that perfluorinated esters are decomposed in the presence of alkali metal fluorides at -78°C or above, but note that for higher molecular weight esters the rate of decomposition at -78°C is slow.

#### Summary of the Invention

Briefly, this invention provides a process for converting even high molecular weight, perfluorinated carboxylic acid esters to perfluorinated acyl fluorides and/or perfluorinated ketones. The process comprises the step of combining at least one perfluorinated carboxylic acid ester with at least one initiating reagent selected from the group consisting of gaseous, non-hydroxylic nucleophiles; liquid, non-hydroxylic nucleophiles; and mixtures of at least one non-hydroxylic nucleophile (gaseous, liquid, or solid) and at least one solvent which is inert to acylating agents. As used herein, the terms "gaseous," "liquid," and "solid" refer to the physical state of the nucleophile under the conditions of temperature and pressure chosen for carrying out the process.

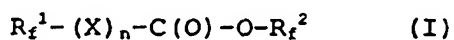
The process of the invention can be carried out at room temperature without the need for high

temperature conditions and special high temperature equipment such as a hot tube. The process also avoids the problem of deactivation associated with the physical occlusion of solid catalysts by tar-forming  
5 contaminants of fluorination processes. Most importantly, the process of the invention enables the dissociation of high molecular weight, perfluorinated esters and is therefore preferably utilized for preparing perfluorinated acyl fluorides and/or  
10 perfluorinated ketones from perfluorinated esters having at least about six carbon atoms. The process is particularly useful for the preparation of alpha-branched perfluorinated acyl fluorides.

15 Detailed Description of the Invention

Perfluorinated esters which can be utilized in the process of the invention are cyclic or acyclic, perfluorinated mono- or dicarboxylic acid esters derived from primary or secondary alcohols. Other  
20 classes of compounds which contain an ester moiety, e.g., carbonates and carbamates, can also be utilized, and, as used herein, the term "ester" includes such classes of compounds. The esters may contain small amounts of fluorinated material having one or a few  
25 residual hydrogen atoms, but are essentially fully fluorinated, i.e., perfluorinated. Preferably, the perfluorinated esters contain at least about six carbon atoms.

A class of perfluorinated esters which can be  
30 utilized in the process of the invention is that which can be represented by the following general formula:

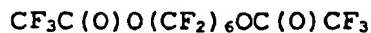
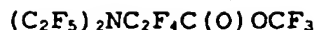


wherein  $R_f^1$  is selected from the group consisting of fluorine; linear, branched, and cyclic perfluoroalkyl groups which have from 1 to about 30 carbon atoms; linear, branched, and cyclic perfluoroalkyl groups which have from 1 to about 30 carbon atoms and which contain at least one catenary, i.e., in-chain, heteroatom (preferably, at least one catenary ether oxygen atom); and linear, branched, and cyclic perfluoroalkylene groups which have from 1 to about 30 carbon atoms and which are bonded to  $R_f^2$  or to an  $R_f^3$  group of X to form a cyclic structure;  $R_f^2$  is selected from the group consisting of linear, branched, and cyclic, primary and secondary perfluoroalkyl groups which have from 1 to about 30 carbon atoms; linear, branched, and cyclic, primary and secondary perfluoroalkyl groups which have from 1 to about 30 carbon atoms and which contain at least one catenary heteroatom (preferably, at least one catenary ether oxygen atom); and linear, branched, and cyclic, primary and secondary perfluoroalkylene groups which have from 1 to about 30 carbon atoms and which are bonded to  $R_f^1$  to form a cyclic structure; X is selected from the group consisting of -O- and -NR<sub>f</sub><sup>3</sup>-, wherein  $R_f^3$  is selected from the group defined above for  $R_f^1$ , with the proviso that when  $R_f^3$  is perfluoroalkylene it is bonded to  $R_f^1$ ; n is an integer of 0 or 1; and wherein  $R_f^1$  or  $R_f^2$  can further contain an ester moiety. A preferred subclass of perfluorinated esters is that represented by general formula I above, wherein  $R_f^1$  and  $R_f^2$  each contain from 1 to about 18 carbon atoms and wherein the sum of the number of carbon atoms in  $R_f^1$  and the number of carbon atoms in  $R_f^2$  is at least about 6.

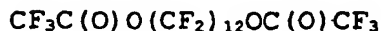
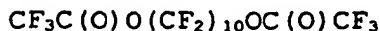
Representative examples of suitable  
perfluorinated esters include the following compounds:

5	$C_3F_7OC(O)C_2F_5$
	$C_5F_{11}C(O)OC_6F_{13}$
	$C_5F_{11}C(O)OCF_3$
10	$C_6F_{13}OC(O)CF_3$
	$C_6F_{13}OC(O)OC_6F_{13}$
15	$C_4F_9CF(C_2F_5)C(O)OCF_3$
	$C_7F_{15}C(O)OCF(CF_3)_2$
	$C_4F_9CF(C_2F_5)CF_2OC(O)CF_3$
20	$C_{16}F_{33}OCOCF_3$
	$C_6F_{13}CF(OC(O)CF_3)CF_3$
25	$(CF_3)_3CC(O)OCF_3$
	$(CF_3)_3CCF_2OC(O)CF_3$
	cyclo- $C_6F_{11}C(O)OCF_3$
30	cyclo- $C_6F_{11}OC(O)CF_3$
	$C_4F_9(OC_2F_4)_2OC(O)CF_3$
	$C_7F_{15}OC_2F_4C(O)OCF_3$

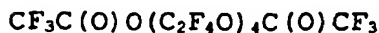




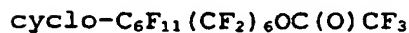
5



10



15



Perfluorinated esters suitable for use in the process of the invention can be prepared by either the direct fluorination or the electrochemical fluorination of the corresponding hydrocarbon or partially-fluorinated carboxylic acid esters, as described, e.g., in U.S. Pat. Nos. 5,093,432 (Bierschenk et al.) and 3,900,372 (Childs et al.).

Suitable hydrocarbon precursors for use in direct or electrochemical fluorination can be prepared by the reaction of alcohols and carboxylic acids (or derivatives thereof, e.g., carboxylic acid chlorides), by the alcoholysis of nitriles, and by other known methods (see, e.g., S. R. Sandler and W. Karo, Organic Functional Group Preparations, Second Edition, Academic Press, Inc., pages 288-314, New York (1983)).

Suitable partially-fluorinated precursors can be prepared, e.g., by the reaction of alcohols with

partially-fluorinated or perfluorinated carboxylic acids (or derivatives thereof), as described, e.g., in U.S. Pat. No. 3,900,372 (Childs), and by the reaction of partially-fluorinated alcohols with carboxylic acids (or derivatives thereof), as described, e.g., by M. Hudlicky, Chemistry of Organic Fluorine Compounds, Second Edition, Ellis Horwood, page 325, New York (1992).

Perfluorinated esters suitable for use in the process of the invention can also be prepared by the reaction of perfluoroacyl fluorides with alkali metal perfluoroalkoxides, as described by De Marco et al. in J. Org. Chem. 37(21), 3332 (1972).

Initiating reagents which can be employed in the process of the invention are those gaseous or liquid, non-hydroxylic nucleophiles and mixtures of gaseous, liquid, or solid, non-hydroxylic nucleophile(s) and solvent (hereinafter termed "solvent mixtures") which are capable of nucleophilic reaction with the perfluorinated esters. A wide variety of materials with modest to strong nucleophilic properties possess such capability and initiate an apparent fluoride-propagated dissociation of the perfluorinated esters into two perfluoroacyl components. The presence of small amounts of hydroxylic nucleophiles can be tolerated.

Suitable gaseous or liquid, non-hydroxylic nucleophiles for use in the process of the invention include dialkylamines, trialkylamines, carboxamides, alkyl sulfoxides, amine oxides, oxazolidones, pyridines, and the like, and mixtures thereof. Suitable non-hydroxylic nucleophiles for use in solvent mixtures include such gaseous or liquid, non-hydroxylic nucleophiles, as well as solid, non-

hydroxylic nucleophiles, e.g., fluoride, cyanide, cyanate, iodide, chloride, bromide, acetate, mercaptide, alkoxide, thiocyanate, azide, trimethylsilyl difluoride, bisulfite, and bifluoride anions, which can be utilized in the form of alkali metal, ammonium, alkyl-substituted ammonium (mono-, di-, tri-, or tetra-substituted), or quaternary phosphonium salts, and mixtures thereof. Such salts are in general commercially available but, if desired, can be prepared by known methods, e.g., those described by M. C. Sneed and R. C. Brasted in Comprehensive Inorganic Chemistry, Volume Six (The Alkali Metals), pages 61-64, D. Van Nostrand Company, Inc., New York (1957), and by H. Kobler et al. in Justus Liebigs Ann. Chem. 1978, 1937. 1,4-diazabicyclo[2.2.2]octane and the like are also suitable solid nucleophiles.

Representative examples of suitable gaseous or liquid, non-hydroxylic nucleophiles include trimethylamine, triethylamine, dimethylformamide, dimethylsulfoxide, N-methyl-2-oxazolidone, pyridine, lutidine, quinoline, and mixtures thereof. Trimethylamine, triethylamine, pyridine, and dimethylformamide (and mixtures thereof) are preferred due to their ready availability.

Representative examples of suitable solid, non-hydroxylic nucleophiles include the fluoride, cyanide, cyanate, iodide, chloride, bromide, acetate, mercaptide, alkoxide, thiocyanate, azide, trimethylsilyl difluoride, bisulfite, and bifluoride salts of lithium, sodium, potassium, ammonium, alkyl-substituted ammonium (where the alkyl group(s) have from one to about ten carbon atoms), tris(dimethylamino)sulfonium, and tetraaryl

phosphonium (where the aryl groups are phenyl or substituted phenyl); 1,4-diazabicyclo[2.2.2]octane; and mixtures thereof. The preferred anions for use in the process of the invention are fluoride and chloride  
5 (due to considerations of cost, availability, and product purity), and these anions are preferably utilized in the form of potassium, sodium, ammonium, or alkyl-substituted ammonium salts, or mixtures thereof.

10 Fluoride ion is the most preferred nucleophile (preferably, in the form of the potassium salt, which is inexpensive and readily available) because it produces acyl fluoride directly, whereas other nucleophiles apparently produce contaminatory and/or  
15 yield-reducing by-products.

The above-cited nucleophiles have the indicated physical states under ambient or room temperature conditions. Since physical states vary with temperature, these or other nucleophiles may be  
20 suitable for use at other temperatures, as is known by those skilled in the art.

Solvents which can be utilized in the process of the invention are those which are inert to acylating agents. Such solvents include polar, aprotic  
25 solvents. Representative examples of polar, aprotic solvents include acyclic ethers such as diethyl ether, ethylene glycol dimethyl ether, and diethylene glycol dimethyl ether; cyclic ethers such as tetrahydrofuran, 2-methyltetrahydrofuran, dioxane, dioxolane, and 4-  
30 methyldioxolane; ketones such as acetone and 2-butanone; carboxylic acid esters such as methyl formate, ethyl formate, methyl acetate, diethyl carbonate, propylene carbonate, ethylene carbonate, and butyrolactones; nitriles such as acetonitrile and

benzonitrile; nitro compounds such as nitromethane or nitrobenzene; alkyl amides such as N,N-dimethylformamide, N,N-diethylformamide, and N-methylpyrrolidone; alkyl sulfones such as  
5 dimethylsulfone, tetramethylene sulfone, and other sulfolanes; oxazolidones such as N-methyl-2-oxazolidone; and mixtures thereof.

Nonpolar, aprotic solvents (e.g., alkanes and arenes) can also be utilized in the process of the  
10 invention in admixture with phase transfer catalyst(s). Representative examples of such solvent/catalyst combinations include toluene/crown ether, e.g., 18-crown-6; toluene/tetraalkylammonium halide, e.g., tetrabutylammonium fluoride;  
15 benzene/tetraarylphosphonium halide, e.g., tetraphenylphosphonium chloride; heptane/crown ether, and the like; and mixtures thereof. If desired, polar, aprotic solvent can be mixed with nonpolar, aprotic solvent or with a mixture of nonpolar, aprotic  
20 solvent and phase transfer catalyst.

Preferred solvents include diethylene glycol dimethyl ether, acetonitrile, acetone, toluene/crown ether, toluene/tetraalkylammonium fluoride, and mixtures thereof. Acetonitrile, diethylene glycol  
25 dimethyl ether, toluene/tetraalkylammonium fluoride, and mixtures thereof are most preferred due to their relatively low cost and/or ease of drying.

The process of the invention can be carried out by introducing at least one perfluorinated ester and  
30 at least one initiating reagent (which may comprise at least one solvent component, in addition to at least one nucleophile component) to a vessel, which can be an open or closed vessel, and which preferably is a stirred reactor connected to separation means (e.g.,

condenser(s) and/or trap(s)) for isolating volatile reaction products and enabling their removal or recycle. The ester and the component(s) of the initiating reagent can be introduced to the vessel  
5 separately or in any manner of combination, and in any order. When the process is carried out on a small scale, the ester can be conveniently added to the vessel first, and the component(s) of the initiating reagent then combined and added to the vessel. The  
10 contents of the vessel is preferably agitated to facilitate mixing.

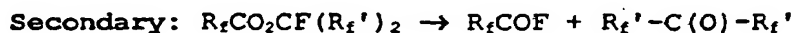
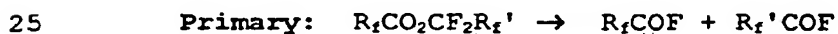
The process of the invention can be generally carried out at a temperature in the range of from about 0°C to about 100°C (depending, e.g., on the  
15 reaction rate desired), but, for convenience, is preferably carried out under room temperature conditions. The nucleophile component (or components) of the initiating reagent is used in an amount sufficient to initiate the dissociation of the  
20 perfluorinated ester. This amount is generally a sub-stoichiometric amount, e.g., amounts as low as a few milligrams of nucleophile per 100 grams of perfluorinated ester have been found to be effective.

The solvent component (or components) of the  
25 initiating reagent, if any, is utilized in an amount sufficient to wet the surface of solid nucleophile. Both the reaction conditions and the proportions of ester, nucleophile, and solvent can vary widely.

The process of the invention can be carried out  
30 continuously (e.g., by continuously feeding perfluorinated ester to the vessel and continuously withdrawing perfluorinated product from the vessel), semi-continuously (e.g., by continuously feeding ester

and intermittently withdrawing product, or by  
intermittently feeding ester and continuously  
withdrawing product), or batchwise. Depending upon  
the degree of purity of the perfluorinated ester, a  
5 single addition of an initiating amount of nucleophile  
can be sufficient or subsequent replenishment can be  
necessary. The process can be carried out with  
recycle of at least a portion of the product  
perfluorinated acyl fluoride(s) (resulting from the  
10 dissociation of the perfluorinated ester) for use in  
preparing partially-fluorinated esters which can be  
fluorinated to provide additional perfluorinated ester  
for use in the process.

The process of the invention enables the  
15 conversion of even high molecular weight,  
perfluorinated carboxylic acid esters to  
perfluorinated acyl fluorides and/or perfluorinated  
ketones. The types of perfluorinated products which  
are obtained in a particular case are dependent upon  
20 the nature of the starting ester, in that esters  
derived from primary alkanols provide different  
products from those derived from secondary alkanols,  
as shown by the following general reaction schemes:



The perfluorinated products of the process of the  
30 invention can be recovered by, e.g., draining and can  
then be separated and purified by, e.g., distillation,  
if desired.

The process of the invention can be carried out at room temperature without the need for high temperature conditions and special high temperature equipment such as a hot tube. The process also avoids the problem of deactivation associated with the physical occlusion of solid catalysts by tar-forming contaminants of fluorination processes. The process is particularly useful for the preparation of alpha-branched perfluorinated acyl fluorides. The perfluorinated products of the process are useful as reactive intermediates for the preparation of monomers, surfactants, and other materials such as textile treating agents, paper treating agents, and potting compounds.

This invention is further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

#### EXAMPLES

##### Example 1

Dissociation of  $n\text{-C}_6\text{F}_{13}\text{O}(\text{CO})\text{CF}_3$  Using a Mixture of Potassium Fluoride and Triglyme

A partially-fluorinated precursor ester,  $n\text{-C}_6\text{H}_{13}\text{O}(\text{CO})\text{CF}_3$ , was prepared by treatment of 510 g of  $n$ -hexanol with 450 mL of trifluoroacetic acid and 50 mL of concentrated  $\text{H}_2\text{SO}_4$ , with overnight stirring at  $23^\circ\text{C}$ . 97 g of the precursor was fluorinated with  $\text{F}_2$  in Freon<sup>TM</sup> 113 (1,1,2-trichloro-1,2,2-trifluoroethane, available from DuPont) using the procedure taught in U.S. Pat. No. 5,093,432 (Bierschenk et al.) to produce



perfluorinated ester,  $n\text{-C}_6\text{F}_{13}\text{O}(\text{CO})\text{CF}_3$ . The Freon<sup>TM</sup> 113 solution of the ester was stripped of solvent using a three-plate Snyder column to yield 134.2 g of crude perfluorinated ester product. The product was mixed  
5 with 30 mL of triglyme (triethyleneglycol dimethyl ether) to which 2 g of KF had been added. Gas (presumed to be trifluoroacetyl fluoride) was immediately evolved, but was not collected. The liquid product, perfluorohexanoyl fluoride, was then  
10 distilled to yield 46.2 g of  $n\text{-C}_5\text{F}_{11}\text{COF}$  having a boiling range of 60-64°C. Samples of the gas and of the liquid product were treated with methanol to provide the methyl esters  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  and  $n\text{-C}_5\text{F}_{11}\text{C}(\text{O})\text{OCH}_3$ , confirmed by gas chromatographic (GC)  
15 analysis.

#### Comparative Example 1

##### Attempted Dissociation of $n\text{-C}_{10}\text{F}_{21}\text{O}(\text{CO})\text{CF}_3$ Using Solid Sodium Fluoride

20 Perfluoro(decyl acetate),  $n\text{-C}_{10}\text{F}_{21}\text{O}(\text{CO})\text{CF}_3$ , was prepared by direct fluorination of 71.2 g of decyl trifluoroacetate, using essentially the procedure of Example 1. 155.2 g of the neat perfluorinated ester was heated to about 150°C with no change, was cooled,  
25 and was then treated with 2 g of solid NaF, but no evolution of gas was observed, indicating that the ester was not cleaved under these conditions. The resulting mixture was then heated to 150°C for approximately 2 hours without any gas evolution. This  
30 comparative example shows that higher molecular weight perfluorinated esters such as perfluoro(decyl acetate) may not cleave upon contact with solid, non-hydroxylic

nucleophile in the absence of solvent, even when heated to temperatures well above room temperature.

#### Example 2

- 5    **Dissociation of  $C_4F_9O(C_2F_4O)_2(CO)CF_3$  Using a Mixture of Potassium Fluoride and Diglyme**

$C_4F_9O(C_2F_4O)_2(CO)CF_3$  was prepared by direct fluorination of 100 g of  $C_4H_9O(C_2H_4O)_2(CO)CH_3$  by essentially the procedure of Example 1. To 243 g of  
10    the resulting crude perfluorinated ester was added 0.5 g of KF in 1 g of diglyme. Gas evolution was observed, indicating ester cleavage. The resulting product was purified by distillation to yield 144.6 g of  $C_4F_9OC_2F_4OCF_2COF$ , boiling at 105-110°C.

15

#### Example 3

- Dissociation of Perfluoro(methyl cyclohexanoate) Using a Mixture of Potassium Fluoride and Diglyme**

Perfluoro(methyl cyclohexanoate) was prepared by  
20    direct fluorination of methyl benzoate, using essentially the procedure of Example 1. To 504 g of the crude perfluorinated ester (assayed at 60% by GC analysis of the methyl ester) was added 1 g of KF in 10 mL of diglyme. After rapid evolution of gas  
25    (presumed to be carbonyl fluoride) was complete, the resulting product was distilled to yield 150.5 g of perfluorocyclohexane carbonyl fluoride, boiling at 78-90°C.

30

#### Example 4

- Dissociation of  $CF_3OC_3F_6OCF_2CF(OC(O)CF_3)CF_3$  Using a Mixture of Potassium Fluoride and Diglyme**

CF<sub>3</sub>OC<sub>3</sub>F<sub>6</sub>OCF<sub>2</sub>CF(OC(O)CF<sub>3</sub>)CF<sub>3</sub> was prepared by direct fluorination of 100 g of dipropyleneglycol methyl ether acetate using essentially the procedure of Example 1. The resulting solution of crude

5 perfluorinated ester was concentrated to 142 g by evaporation of most of the solvent. The resulting concentrate was treated with 0.2 g of KF in 2 mL of diglyme, resulting in vigorous evolution of gas (presumed to be trifluoroacetyl fluoride). When gas

10 evolution ceased, the resulting product was distilled using a 6-inch Vigreux column to yield 88.9 g of perfluorinated ketone, CF<sub>3</sub>OC<sub>3</sub>F<sub>6</sub>OCF<sub>2</sub>C(O)CF<sub>3</sub>, boiling at 85°C. The product was confirmed by IR analysis.

15 Example 5

Dissociation of Perfluoro(ε-caprolactone) Using Pyridine

Perfluoro(ε-caprolactone) was prepared by direct fluorination of 97.3 g of ε-caprolactone using

20 essentially the procedure of Example 1. The resulting solution of crude perfluorinated ester was concentrated to about 300 g by evaporation of most of the solvent. A 50 g sample of the resulting concentrate was treated with 2 drops of pyridine,

25 resulting in a moderate exotherm and complete conversion of the ester to perfluoroadipoyl fluoride, as confirmed by IR and GC analysis of the dimethyl ester.

30 Example 6 and Comparative Example 2

Dissociation of Perfluoro(dimethyl tricyclo[1.1.1]pentane-1,3-dicarboxylate) Using a

Mixture of Potassium Fluoride and Diglyme and a  
Mixture of Potassium Iodide and Acetone

Perfluoro(dimethyl tricyclo[1.1.1]pentane-1,3-dicarboxylate) was prepared by direct fluorination of  
5 dimethyl tricyclo[1.1.1]pentane-1,3-dicarboxylate,  
using essentially the procedure of Example 1. About 1  
mL of the neat perfluorinated ester was first shaken  
with approximately 10 mg of solid KF as a comparative  
example, and no gas evolution was observed. A drop of  
10 diglyme was then added to the mixture of ester and KF  
(according to the process of the invention), and  
evolution of gas (presumed to be carbonyl fluoride)  
ensued. Cleavage of the diester to the diacyl  
fluoride was confirmed by IR analysis.

15 The above procedure was repeated using about 5  
drops of a 5% (weight to volume) solution of KI in  
acetone and about 1 mL of the ester. Again, evolution  
of gas (presumed to be carbonyl fluoride) was  
observed, and cleavage was confirmed by IR analysis.

20

Example 7

Dissociation of Perfluoro(hexanediol diacetate) Using  
Pyridine

Perfluoro(hexanediol diacetate) was prepared by  
25 direct fluorination of hexanediol diacetate, using  
essentially the procedure of Example 1. The resulting  
crude perfluorinated diester was concentrated by  
evaporation of solvent. One mL of the concentrated  
diester was treated with one drop of pyridine, and  
30 immediate evolution of gas (presumed to be  
trifluoroacetyl fluoride) was observed. Complete  
conversion of the perfluorinated diester to the

perfluorinated diacyl fluoride, perfluoroadipoyl fluoride, was confirmed by IR analysis.

Examples 8-11 and Comparative Examples 3-6

5    **Dissociation of Various Perfluorinated Esters Using a Mixture of Potassium Fluoride and Diglyme**

          A number of additional perfluorinated esters were cleaved using the process of the invention. In each case, a small sample (about 1 mL) of the neat  
 10    ester was first shaken with a few milligrams of solid KF (in a glass vial) as a comparative example. No gas evolution was observed for any of the esters, so a drop of diglyme was then added to the mixture of ester and KF (according to the process of the invention),  
 15    and the resulting mixture was shaken. In each case, gas evolution was then observed and was taken as evidence that the ester had been cleaved to acyl fluoride. Such cleavage was confirmed by IR analysis. The perfluorinated esters cleaved are listed in Table  
 20    1 below:

Table 1

Example No.	Perfluorinated Ester
8	$n\text{-C}_{10}\text{F}_{21}\text{O}(\text{CO})\text{CF}_3$
9	$(\text{CF}_3)_3\text{CC}(\text{O})\text{OCF}_3$
10	4-Cl-cyclo- $\text{C}_6\text{F}_{10}\text{OC}(\text{O})\text{CF}_3$
11	$\text{C}_4\text{F}_9\text{CF}(\text{C}_2\text{F}_5)\text{CF}_2\text{OC}(\text{O})\text{CF}_3$

Example 12

Dissociation of  $C_6F_{13}CF[OC(O)CF_3]CF_3$  Using a Mixture of Potassium Fluoride and Diglyme

5  $C_6F_{13}CF[OC(O)CF_3]CF_3$  was prepared by direct fluorination of 100 g of 2-octyl acetate, using essentially the procedure of Example 1. The resulting crude perfluorinated ester was distilled to provide 267 g of perfluorinated ester, to which a mixture of 10 2.0 g of KF and 5 mL of diglyme was added. Gas evolution was observed. The resulting mixture was stirred overnight and then distilled to yield 151.5 g of perfluoro(2-octanone), boiling at 101-109°C. The product was confirmed by IR analysis.

15

Examples 13-27 and Comparative Examples 7-12

Dissociation of Perfluoro(nonyl acetate) Using Various Different Initiating Reagents

A partially-fluorinated precursor ester, nonyl 20 trifluoroacetate, was prepared by dropwise addition of 170 mL of trifluoroacetic acid to 290 g of n-nonanol, followed by addition of 22 mL of concentrated  $H_2SO_4$ . The resulting mixture was stirred at 60°C overnight. The stirred mixture was then cooled, the resulting 25 organic phase was collected, and partially-fluorinated ester product was isolated by distillation (bp 49-56°C/0.1 torr). The product was then fluorinated in Freon™ 113 by essentially the procedure of Example 1 to provide perfluoro(nonyl acetate),  $C_9F_{19}O(CO)CF_3$ .

30 A number of different initiating reagents were evaluated by adding a small amount of reagent to approximately 1 mL of neat perfluoro(nonyl acetate). The "small amount" was a few milligrams for solid

reagents, a drop for liquid or solution reagents, and a few small bubbles for gaseous reagents. Cleavage of the perfluorinated ester to perfluorononanoyl fluoride was first determined by observed gas evolution (presumed to be trifluoroacetyl fluoride) and was then verified by IR analysis. The results of the evaluations are shown in Table 2 below and indicate that perfluorinated esters can be cleaved by a variety of initiating reagents comprising non-hydroxylic nucleophile in gaseous, liquid, or solvent mixture form.

Table 2

Example No.	Initiating Reagent	Cleavage to C <sub>9</sub> F <sub>17</sub> COF
13	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	Yes
14	Pyridine	Yes
15	Dimethylformamide	Yes
Comparative 7	NaF	No
16	NaF/Diglyme	Yes
Comparative 8	NH <sub>4</sub> F	No
17	NH <sub>4</sub> F/CH <sub>3</sub> CN	Yes
18	NaI/Acetone	Yes
19	NaN <sub>3</sub> /Acetone	Yes
20	NaF/CH <sub>3</sub> CN	Yes
21	KF/18-crown-6 Ether/Toluene	Yes
22	NaCl/18-crown-6 Ether/Benzene	Yes

Example No.	Initiating Reagent	Cleavage to C <sub>8</sub> F <sub>17</sub> COF
23	KBr/18-crown-6 Ether/Benzene	Yes
24	(CH <sub>3</sub> ) <sub>2</sub> NH	Yes
Comparative 9	CH <sub>3</sub> CN	No
Comparative 10	Water	No
Comparative 11	Methanol	No
Comparative 12	Ethanol	No
25	Ethyl oxazoline	Yes
26	Adogen <sup>TM</sup> 464 *	Yes
27	Sodium Acetate/Acetone	Yes

\* Adogen<sup>TM</sup> 464 is a mixture of methyl trialkyl (C<sub>8</sub>-C<sub>10</sub>) ammonium chlorides available from Aldrich Chemical Company.

5

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

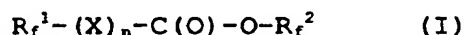


Claims

1. A process for converting perfluorinated  
5 carboxylic acid esters to perfluorinated acyl  
fluorides and/or perfluorinated ketones comprising the  
step of combining at least one perfluorinated  
carboxylic acid ester with at least one initiating  
reagent selected from the group consisting of gaseous,  
10 non-hydroxylic nucleophiles; liquid, non-hydroxylic  
nucleophiles; and mixtures of at least one non-  
hydroxylic nucleophile and at least one solvent which  
is inert to acylating agents.

15 2. The process of Claim 1 wherein said ester has  
at least about six carbon atoms.

3. The process of Claim 1 wherein said ester is  
selected from the group represented by the general  
20 formula



wherein  $R_f^1$  is selected from the group consisting of  
25 fluorine; linear, branched, and cyclic perfluoroalkyl  
groups which have from 1 to about 30 carbon atoms;  
linear, branched, and cyclic perfluoroalkyl groups  
which have from 1 to about 30 carbon atoms and which  
contain at least one catenary heteroatom; and linear,  
30 branched, and cyclic perfluoroalkylene groups which  
have from 1 to about 30 carbon atoms and which are  
bonded to  $R_f^2$  or to an  $R_f^3$  group of X to form a cyclic  
structure; said  $R_f^2$  is selected from the group  
consisting of linear, branched, and cyclic, primary

and secondary perfluoroalkyl groups which have from 1 to about 30 carbon atoms; linear, branched, and cyclic, primary and secondary perfluoroalkyl groups which have from 1 to about 30 carbon atoms and which contain at least one catenary heteroatom; and linear, branched, and cyclic, primary and secondary perfluoroalkylene groups which have from 1 to about 30 carbon atoms and which are bonded to said  $R_f^1$  to form a cyclic structure; said X is selected from the group consisting of -O- and -NR<sub>f</sub><sup>3</sup>-, wherein R<sub>f</sub><sup>3</sup> is selected from the group defined above for said R<sub>f</sub><sup>1</sup>, with the proviso that when said R<sub>f</sub><sup>3</sup> is perfluoroalkylene it is bonded to said R<sub>f</sub><sup>1</sup>; and n is an integer of 0 or 1.

15

4. The process of Claim 3 wherein said R<sub>f</sub><sup>1</sup> or said R<sub>f</sub><sup>2</sup> further contains an ester moiety.

5. The process of Claim 1 wherein said initiating reagent is selected from the group consisting of dialkylamines, trialkylamines, carboxamides, alkyl sulfoxides, amine oxides, oxazolidones, pyridines, mixtures thereof, and mixtures of at least one thereof and at least one said solvent.

20

6. The process of Claim 1 wherein said initiating reagent is selected from the group consisting of mixtures of at least one compound, selected from the group consisting of 1,4-diazabicyclo[2.2.2]octane and the alkali metal, ammonium, alkyl-substituted ammonium, tris(dimethylamino)sulfonium, and quaternary phosphonium salts of fluoride, cyanide, cyanate,

30

iodide, chloride, bromide, acetate, mercaptide, alkoxide, thiocyanate, azide, trimethylsilyl difluoride, bisulfite, and bifluoride anions, and at least one said solvent.

5

7. The process of Claim 1 wherein said solvent is selected from the group consisting of polar, aprotic solvents; mixtures of at least one nonpolar, aprotic solvent and at least one phase transfer catalyst; mixtures of at least one polar, aprotic solvent and at least one nonpolar, aprotic solvent; and mixtures thereof.

8. The process of Claim 1 wherein a sub-stoichiometric amount of said initiating reagent is utilized.

9. The process of Claim 1 carried out at a temperature in the range of from about 0°C to about 100°C.

10. A process for converting perfluorinated carboxylic acid esters to perfluorinated acyl fluorides and/or perfluorinated ketones comprising the step of combining at least one perfluorinated carboxylic acid ester having at least about six carbon atoms with at least one initiating reagent selected from the group consisting of trimethylamine; triethylamine; pyridine; dimethylformamide; mixtures of at least one salt, selected from the group consisting of the potassium, sodium, ammonium, and alkyl-substituted ammonium salts of fluoride and chloride anions, and at least one solvent selected

from the group consisting of acetonitrile, diethylene glycol dimethyl ether, and toluene/tetraalkylammonium fluoride; and mixtures thereof.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/01995

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6 C07C51/60 C07C51/58 C07C53/50 C07C55/40 C07C59/135 C07C51/215 C07C45/54 C07C49/175		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6 C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 557 167 (MINNESOTA MINING AND MANUFACTURING CO.) 25 August 1993 see page 8, line 25 - page 10, line 31 see claims 1,8,9 ---	1-7,10
A	JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS, no.13, 4 July 1973, LETCHWORTH GB page 425 D.J.BURTON ET AL. 'DIRECT CLEAVAGE OF ESTERS TO ACID HALIDES.' THE WHOLE ARTICLE. --- -/--	1
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search  19 May 1995		Date of mailing of the international search report  - 1. 06. 95
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tlx. 31 651 epo nl, Fax (+ 31-70) 340-3016		Authorized officer  Klag, M

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/01995

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF ORGANIC CHEMISTRY., vol.44, no.13, 22 June 1979, EASTON US pages 2291 - 2292 W.J.MIDDLETON 'ONE-STEP METHOD FOR CONVERTING ESTERS TO ACYL CHLORIDES.' THE WHOLE ARTICLE. -----	1
A	EP,A,0 048 544 (E.I.DU PONT DE NEMOURS & CO.) 31 March 1982 see claim 1 -----	1

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No  
PCT/US 95/01995

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0557167	25-08-93	CA-A- 2087390	13-08-93
		CN-A- 1075313	18-08-93
		JP-A- 6040951	15-02-94
-----			
EP-A-0048544	31-03-82	US-A- 4316986	23-02-82
		JP-C- 1264276	16-05-85
		JP-A- 57098226	18-06-82
		JP-B- 59040376	29-09-84
-----			

